TRANSPORTATION RESEARCH BOARD
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IDEA *Innovations Deserving Exploratory Analysis Project*

NATIONAL COOPERATIVE HIGHWAY RESEARCH PROGRAM

Report of Investigation

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Laser Removal of Paint on Pavement

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INNOVATIONS DESERVING EXPLORATORY ANALYSIS (IDEA) PROGRAMS
MANAGED BY THE TRANSPORTATION RESEARCH BOARD (TRB)

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IDEA PRODUCT

A prototype portable laser for removal of paint from the pavement highways, parking lots, and airfield runways will be developed. Its impact will be (a) the elimination of the usual environmental contaminants such as grit, dust, smoke, and chemicals; (b) prevention of damage to pavement during paint removal; and (c) completion of removal for compliance with federal codes that require no visible trace of temporary markings on newly constructed roadways.

CONCEPT AND INNOVATION

Lasers typically remove paint by heating, charring, and slow burning with air or an oxygen jet. This approach causes pollution, damage to asphalt, and it is too expensive to be viable commercially. Another approach is the use of a succession of short, intense, laser pulses that create destructive shock waves rather than heating to the point where chemical reactions occur and smoke is generated. There is also a need for reconditioning the surfaces of certain types of markings so that additional markings can be applied adherently. We have tested several types and brands of lasers to demonstrate such removal of a number to paint types in the laboratory. This provided data for optimizing the important laser variables: wavelength, pulse duration, and extent of focusing. We then mounted a laser on a self-propelled cart and demonstrated mobile paint removal. The innovation will be complete when we are able to put durable, high-power mobile lasers safely in the field for paint removal and surface conditioning.

IDEA PROJECT INVESTIGATION AND PROGRESS

This project is best described by four stages of investigation. They are:
1. investigation of paint properties to better design a removal method,
2. statistically designed laser experiments to identify the important variables,
3. optimization of the method and equipment in the laboratory, and
4. field-tests with a laser on a mobile carriage.

Stage 1. Paint Properties

The objective is to break the chemical bonds that attach paint or marking material to the substrate. By calculating the bond density and assuming that about 100 kJ/mole of bonds will be required for breakage. we can show that the energy is only 1.7 x 10-3 J/cm^2 if all of the applied energy is placed at the interface of the marking and substrate. Initially we hoped that we could select a near-infrared wavelength that would penetrate paint and would be absorbed by underlying black asphalt. Liu and Garmire (1) have established that the 1.06 m laser wavelength is as good or better than other wavelengths for the removal of thin spray paint, so we felt safe in using the same wavelength for road paint. Lasers that have neodymium ions embedded in yttrium aluminum garnet emit this wavelength. They are abbreviated Nd:YAG lasers.

If this infrared light is transmitted by the paint but absorbed strongly by the asphalt, it would concentrate the energy where we wanted it—right at the paint-substrate interface. In a matter of microseconds, the interface would heat to over 100°C which causes outgasing of the paint matrix. This rapid rise of gas pressure could blow a chip of paint off the roadway. To better control this process, we investigated certain properties of some typical roadway marking paints, including lacquers and water based marking paints.

By slowly heating chips of dried lacquer (Bauer UN1263) in an enclosed tube, we were able to drive off gas from the paint, and to identify the gases in the mixture using infrared spectroscopy. At 80°C, the ratio of gas volume to solid paint volume is 1.2. This gas was primarily air, water, and carbon dioxide, none of which are objectionable as emissions from this process. The paint is beginning to soften at this temperature.

At 120°C, the volume ratio was 2.3 and more noxious gases were being emitted (e.g., hydrochloric acid, oxides of nitrogen, and chlorinated organic hydrocarbons). At this temperature, the paint was a viscous liquid surrounding many small, solid particles.

The volume ratio got as high as 13.6 at 141°C. Upon cooling, a brown liquid condensed from the gas. This was shown to be a chlorinated organic compound. We conclude that there is sufficient gas condensed in the paint to expand upon rapid heating and thereby remove overlying paint. If the temperature is kept below about 100°C, the gases are not noxious and the paint remains brittle. Hotter paint would form bubbles rather than fly off as chips.

We investigated the porosity of paint to see if the self-generated gas could escape before building up sufficient pressure. Although the UN1263 paint was rather porous, a 0.57-mm thick layer took more than 3 minutes to release a differential air pressure of 4 millibar. According to Poiseuille's Law, the flow through a pore is proportional to the 4^{th} power of the radius of the pore, so this implies that the pores in this paint were very small. It appears that porosity will not impede paint removal if heating times are short (sub-millisecond).

To test this mechanism, we trapped the evolved gas under about 0.5 mm of paint (Bauer 1231 yellow). We did this by applying the paint to glass, drying it, and then irradiating the paint-glass interface through the glass with 0.5 J of laser energy in a 4 ns pulse. Energy absorption occurred at the interface. The paint in a 1-cm diameter circle flew off as a chip, apparently because of gas generated at the interface. The threshold for paint removal was less than 1.6 J/cm^2, which is about 1000 times as much as the energy required breaking only the chemical bonds at the interface. Much of the energy went into unproductive channels that did not directly break the paint/substrate bonds (e.g., reflection, absorption deeper in the paint, heating the substrate, etc.).

Of course the laser energy cannot go from the bottom up on roadways (i.e., through the asphalt to the paint interface). The paint must be irradiated from the top (air interface) down, and the laser parameters need to be optimized for this process. We still hoped to directly heat the paint-substrate interface on the first laser shot. To improve our chances of doing this, we selected the best wavelength for passing though materials. This infrared wavelength, 1.06 m, is too long to excite electronic transitions and two short to excite molecular vibrations; so we hoped the light would penetrate the paint from the top and be absorbed in the first asphalt it reached. Our experiments showed that this did not occur. The primary problem was multiple scattering of the laser photons by the solid opacifier particles in the paint. These were mainly chalk particles, but other materials such as titanium dioxide also scatter this light. Most of the light was scattered back out of the surface of the paint, so only a thin layer was illuminated by the laser.

The paint still absorbed some of the 1.06 m light, mostly in infrared overtone and combination absorption bands. At low light intensities, the absorbed light warms the paint over a period of milliseconds. We would like to avoid this for two reasons: (1) the paint softens and will not chip off as desired, and (2) at temperatures above about 100°C road paints emit unwanted gases. We therefore chose to work with short-pulse lasers, in which each pulse would chip off a thin (less than 0.1 mm) layer of paint. Our laboratory results showed that removal was clean, but it would require an impracticably large laser to remove a painted line at a rate of 1 mile per 8 hours. Such a rate would compete well with the current sandblasting and grinding methods.

Stage 2. Variable Identification

The best figure of merit for laser removal of paint is the volume of paint removed per joule of laser energy incident on the paint. We will label this V_J and use the units of mm3/J. In an effort to maximize V_J, we must investigate the factors that are most likely to influence its value. We have already shown that one of the best wavelengths is 1.06 m, and we prefer pulses in the nanosecond range. Other possible variables were included in a statistical design that would reveal which of them were important and would reveal the interactions between them (2). Several levels of each variable were used, and the level of every variable for a given experimental plate was selected randomly. Thirty concrete tiles were made and twenty were treated according to the statistical design. Some were etched to improve physical bonding at the surface, and some were sprayed with mold release to decrease the bonding of the paint. The tiles were spray-painted with UN 1263 lacquer. In some cases an asphalt solution was added to increase light absorption by the paint. Some painted tiles were sealed with a solution of polyvinyl alcohol and sodium borate that penetrates pores and then gels. Others were wetted with water immediately before being exposed to the laser. In any case, each tile was drawn through the pulsed, focusing laser beam so that the light dose increased dramatically from one side of the tile to the other. From this, V_J could be measured for various degrees of focusing and various numbers of pulses at a given point. Plotting these sorted data as cumulative probability gave a relatively straight line which showed that all of the variation was due to random statistical error, and not to the changes in the levels of any of the variables. Actually two points were high and corresponded to thicker paint. Each variable will be mentioned, but not discussed in much detail below, because the results did not provide much guidance.

- Paint thickness should have no effect on V_J if each pulse takes off only a portion of the total thickness. Nevertheless, V_J was a little higher for the samples with thicker paint. We attribute this to the thick paint having worse mechanical properties, possibly because during drying, the surface hardened before the lower portion was finished shrinking. This would lead to residual stress.

- Paint brittleness is determined by the temperature of the paint. The polymer matrix has a glass transition temperature of about 100°C. Ablation does not occur at high temperatures where the paint is soft. We found that cooling to dry-ice temperatures had no impact on V_J. This implies that the paint is sufficiently brittle up to at least 40°C, and that the heat removed by cooling does not need to be restored by the laser before ablation can take place.
- Paint absorption of light is determined by its color. Our addition of asphalt increased the absorption of light from about 3% to about 8%. However, this did not improve V_J. Apparently the laser energy is deposited in a way that is largely independent of initial paint absorbance. Even a thin coating of black spray paint made no difference to V_J.
- Paint porosity could be important if outgasing below the surface helps to dislodge paint chips. One would expect that plugging the pore would allow more build up of pressure and better paint removal. This was not the case. Apparently very little outgasing occurs at depths approaching 0.1 mm.
- Paint adhesion is important if removal occurs at the paint-substrate interface. Neither etching nor release films made any difference to V_J. Of all the laser pulses striking a point, apparently only the last few interact with the interface in a way that detaches paint. All of the early pulses ablate upper portions of the paint without affecting the interface.

Stage 3. Optimization

At this point we had isolated the two important variables—incident intensity and pulse duration. This assumes that the treatment does not raise the paint above its glass transition temperature, which is easy to assure if the pulse repetition rate is less than about 100 Hz at each point. Our task now is to find the best combination of intensity and pulse duration.

Although intensity and pulse duration interact during ablation, we can outline the primary effects of each separately. For a given laser beam, the intensity incident on the paint can be increased by focusing, or decreased by expanding the beam with a negative lens. We adjusted the beams of several laboratory lasers in both ways to establish the intensity threshold, I^{th}, where ablation begins, and also the higher intensity where V_J is maximized and begins to decrease.

Low intensity light is about 92% reflected by white road markings, so getting the laser energy into the paint is very inefficient. What little light is absorbed is governed by the Beer-Lambert law, which implies some deep warming of the paint. Fortunately, at the high intensities used in our experiments, light is absorbed by entirely different mechanism. It is far more efficient in coupling the energy into the paint, and it does not deposit much energy deep in the paint, so softening does not occur. In this mechanism, it appears that the leading edge of the pulse generates some free electrons near the surface. This can occur by multi-photon absorption or by dielectric breakdown. Before the pulse ends, these electrons are accelerated to sufficient energy that they knock electrons off atoms during collisions. These new electrons also absorb energy and are accelerated so they too cause further ionization. The resulting electron avalanche soon absorbs the remainder of the laser pulse in a thin layer near the surface of the paint. The temperature becomes very high (600 to 750°C), but cooling by expansion and radiation is so fast that virtually no chemical bonds are broken and virtually no unwanted emissions occur. However, the rapid expansion caused by this heating creates a shock wave (3). The shock is strong enough to pulverize up to 0.1 mm of paint. The following rebound blows the fragments away from the surface. The ablated paint chips are sub-millimeter if they come from thick, well-cured paint, but they can be more than a millimeter in diameter if the paint is thin and not well attached to the substrate.

Our data on the threshold intensity shows it to be in the range of 50 MW/cm^2 to 150 MW/cm^2. Each of the 4 brands of Nd:YAG lasers we tested reached this intensity in the raw beam and could even be defocused to some extent. It should be remembered that barely perceptible ablation occurs at threshold, so V_J will be negligibly small. Increasing the intensity by focusing is helpful up to a point. There is a practical limit, and an absolute upper limit. At very high intensities, the laser will cause air breakdown (electron avalanche) in the air, and absorb or reflect all of the energy before it reaches the paint. At somewhat lower intensities, a plasma forms at the surface of the paint and grows outward at a rate of about 5 x 105 cm/sec (4). Its shock ionizes the ambient air, and this shields the paint. After 200 ns, the shock front is about 1.5 mm away from the paint, and this appears to be more than enough distance to protect the paint. This implies that the end of a long-duration pulse will be wasted. Figure 1 shows the type of response that can be inferred from our data and from the literature (5). It is clear that there is an optimum range of intensities (near the line of maximum slope from the origin) and, by implication, optimum pulse durations since intensity is energy/cm^2 times duration. There will therefore be an optimum range of pulse durations.

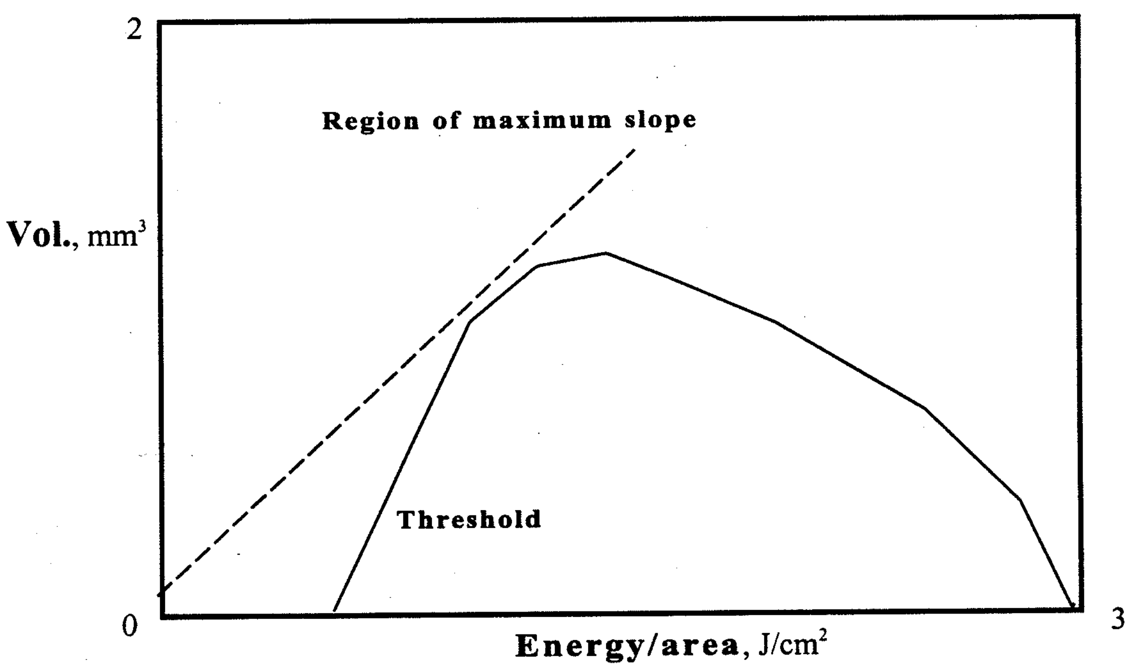

FIGURE 1. Volume of paint removed as a function of incident energy density.

Very short pulses appear to deposit their energy in superthermal electrons which speed outward without effectively depositing their recoil in a shock wave in the paint. The 3.5 ns pulse length of the Coherent Infinity laser we used may have started into this regime. It had lower values for V_J than did the CFR 800 laser (Big Sky Laser Technology) which had a 15 ns pulse length. We were not able to test lasers with longer pulse durations, but it is clear that 200 ns is much too long. In addition, long-duration pulses require focusing to a smaller area to reach the threshold intensity. Of course, area reduction will reduce the volume removed, so focusing can become detrimental. We are convinced that the best range of pulse durations is about 5 to 50 ns. Not many lasers emit pulses in this range, but Q-switched Nd:YAG lasers do. The only other prospective laser is the carbon dioxide laser. It is more electrically efficient but its pulses are much too long (about 1000 ns).

We also note that V_J is not strongly dependent on paint type. Even the durable markings such as hot polymer, cold polymer, and epoxy are removed at approximately the same rate as typical pavement paints. In contrast, polymer below its glass transition temperature (e.g., plastic electrical tape) is not ablated to any extent by the lasers we tried.

The laboratory tests showed feasibility and helped define the optimum laser characteristics, but there were still questions that needed to be answered in field tests. These questions include:

- Will the laser still operate if attached to a vibrating carriage, or will the cavity mirrors become quickly misalign?
- Can the laser beam be scanned across the paint stripe while the carriage moves along the line?
- Will the operator be able to observe and control the position and rate of paint removal?
- Can the operation parameters be changed from paint removal to the type of polymer ablation that reveals more glass beads and restores retroreflectivity?
- Can the laser operation be made safe for the operator and bystanders?

Stage 4. Field Test

Spectra Physics, Inc. allowed us to test one of their large Nd:YAG lasers on a mobile vehicle we had adapted for this use. The vehicle was a hand-operated machine made by 3M company for applying tape markings to roadways. It looked much like a larger, power mower for lawns, but it had an open center portion if there was no tape aboard. The machine was powered by a 5.5-HP gasoline engine that was attached to the wheels with a slip clutch.

A Quanta Ray 7000 laser was strapped to the vehicle. This pulsed laser was operated at 10 Hz. Each pulse was about 10 ns in duration and had an energy of more than 1.0 J. The beam diameter was 1.0 cm and of super-Gaussian profile. Specifically, 85% of the beam profile could be fit with a Gaussian curve. This implies that the center of the beam is more intense than the outer annulus, and this outer region may not have sufficient intensity to reach threshold for paint removal. As with other lasers, changes in the internal optics will adjust the profile to a top-hat shape (same intensity across the entire beam), but this was not practical for these tests even though it is the preferred working profile.

This laser is rather large (about 42 inches long), so it was placed across the vehicle with the laser output extending beyond the right (starboard) side of the carriage. We anticipate the use of much smaller lasers in the future, and the beam may be directed down through the center of the carriage rather than off one of the sides. In the current version, the laser beam was reflected toward the ground by a multilayer mirror that would not be damaged by the high intensity light. We later found that the mirror did not meet the 99% reflection specification, but reflected 7.4% of the light downward. This implies that we would have obtained the same or better removal rate with a 2-watt laser and a 99% mirror.

The mirror was rotated back and forth by about 3 degrees around an axis that was parallel to the painted line. This mechanism swept the beam back and forth across the painted line. The rate could be adjusted, and the best rate for this particular mechanical arrangement was close to 2 Hz. Much faster rates were tried, but the resulting rotational inertia caused too much dwell time at the edges of the paint and not enough time in the center. While scanning, the unit could be moved along the line either by hand or by the gasoline engine that was mounted on the unit. Figure 2 shows a photo of motion variation that cleaned the paint at the slower speeds (about 0.2 cm/s), but removed only the edges at higher speeds (about 1.5 cm/s).

Figure 2. Photograph of paint removal across a stripe (i.e., vertical in the photograph) showing that slow motion is effective and faster carriage motion leaves paint. The mirror scans horizontally in this diagram.

There was some concern that the vibration of the engine would degrade the performance of the laser, but this was proven not to be the case. The Quanta Ray laser we used was a laboratory laser, and not designed for highway use. Smaller Nd:YAG lasers are, e.g., the INDI series from Spectra Physics or the CFR 800 from Big Sky Laser Technologies, Inc. Nevertheless, the Quanta Ray was a good laser for these tests because the raw beam had approximately the right intensity without focusing by any lenses.

This removal unit was videotaped as it removed painted lines from the parking lot of Spectra Physics. The lot had been resurfaced and painted about 2 weeks earlier, probably with Sherwin Williams Water Borne Traffic Marking Paint, which is a white acrylic latex. The lines were 10-cm wide. As expected, paint removal was slow compared to sand blasting or grinding, but removal was clean. The laser generated surprisingly large paint chips; many were 3-mm in diameter. The sealer that covered all of the asphalt came off with the paint. In other words, the fracture occurred between the seal and the asphalt, not between the seal and the paint. The large chips came from within 2 cm of either edge of the painted stripe. Apparently, the paint was thinner there and easier to remove. In fact, sometimes a single pulse would remove the paint in this region. This may have occurred by the outgasing mechanism suggested earlier. The paint was thin enough to allow the sealer or the asphalt to be heated enough to generate gas. In contrast, the central part of the stripe was much more difficult to remove, presumably because its thick paint was stopped light from reaching the seal coat.

Unfortunately, the nature of our mirror scanner exacerbated this problem rather than providing some compensation. The mirror was driven by an electrical handsaw, which apparently converted the rotation of its motor shaft to reciprocal linear motion, by a takeoff that was off-center with respect to the spinning wheel. This makes the reciprocal motion sinusoidal in time, causing more dwell at the edges of the paint, and rapid crossing of the center. In order for the operator to remove the center of the stripe, he had to move along the stripe slowly. This severely overdosed the edges of the stripe and visibly ablated some of the asphalt. However, we did establish the fact that the unit could remove a painted line by a combination of scanning and slow propulsion along the line. For subsequent experiments, the scanning mechanism was turned off so that measurements could be made on a single line of laser spots going in the direction the laser was moving. We could then accurately calculate the dose, in J/cm^2 and measure the associated paint-removal depth. For some experiments, we removed the mirror entirely so its efficiency would not complicate the calculations.

For some experiments, we directed the laser onto a sheet of polymer marking material that had been removed from a roadway after it had become dull from loss of glass beads at its surface. Even at 80% of maximum intensity, the laser ablated some polymer and enhanced the retroreflection from the beads.

The results of these experiments allow us to answer most of the questions, which were stated at the beginning of this section.

- The laser operation was not degraded by the vibration of the gasoline engine.
- The beam scanned the painted line repeatedly, but the current drive mechanism was seriously

mismatched with the thickness of the paint from edge to center. We need a scanning mechanism that can be adjusted for the lateral variations in thickness that are likely to be encountered in the field.

- The operator wore laser safety glasses, but he could see clearly just where paint removal was occurring and whether the removal was complete in that area. He was then able to adjust the speed of the carriage to obtain the desired degree of removal.
- By moving the unit faster, the mode of operation was easily changed from paint removal to restoration of polymer retroreflectivity. Laser intensity was more than adequate, and for later versions of the unit, we should expand the beam with a lens to increase efficiency.
- Although no personal injury occurred (or was even threatened) during these experiments, safety standards for roadway use were far from being met. However, the technical people at Spectra Physics assured us that it would be easy to install shrouds to make the laser beam inaccessible to personnel. If we also added interlocks that turned the laser off if the shroud were lifted from the road, then federal safety standards would be met.

The removal rate was not optimized for the Quanta Ray laser—the objective was to test compatibility with the gasoline-powered carrier, not a measurement of removal speed.

There was more smoke than was necessary for this process. Small chips may have still been in the air when the next laser pulse arrived. These chips absorb light and are unable to get rid of the resulting heat by conduction into the substrate. As a result, they burn in the beam above the surface creating smoke and unwanted gases. What is more, they waste energy that could be used for further paint removal. It is clear that an airstream that removed chips would be beneficial. In addition, a vacuum that caught them and filtered any residual smoke would also be helpful. It should be remembered that the laser beam would be enclosed for safety reasons, so a design for airflow needs to be incorporated in the laser beam housing.

PLANS FOR IMPLEMENTATION OF IDEA RESULTS AND PRODUCT

The best route to commercial viability for this mobile laser unit is to demonstrate its operation in the field. We are preparing a video as a sales tool (different from the video accompanying this report). It will be used to interest potential customers, but ultimately we must allow the customer to operate a prototype of the unit to demonstrate its ability to meet his or her specifications. This implies that we will construct an attractive prototype that incorporates the following improvements:

- Mount the laser head, power supply, cooling system, and a generator in a truck in such a way that the enclosed laser beam goes through the floor of the truck and strikes the road where it can be observed by an operator through a window made of laser safety glass.
- Equip the truck with a double reduction gear so it can be driven down the road at a rate appropriate for the surface-conditioning rate of the laser.
- Use galvanometer-driven laser mirrors and photoelectric feedback to gauge the degree of paint removal and automatically cause the laser to continue pulsing a given position until it is finished.
- Install an air jet to blow debris out of the laser beam, and couple it to a vacuum system to collect

paint chips and reduce smoke pollution.

We expect this prototype to be somewhat expensive (well over $100,000), so we will use our current data and videotape to attract one or more partners to help financially and technically in this endeavor. Likely candidates are paint and marking companies and distributors of highway maintenance equipment. We hope the prototype will generate orders for commercial units, which we will start to build upon reception of firm orders.

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